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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

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INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP97/01568	3/27/97	4/9/96

TITLE OF INVENTION: NEW INSECTICIDE SUSPENSION CONCENTRATES

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [ ] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [ ] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Aplication under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [X] A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [ ] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [ ] Other items or information:

Novel insectidical suspension concentrates

The present invention relates to novel aqueous suspensions of insecticidally active compounds.

When using sparingly water-soluble active compounds in the form of water-diluted sprays, it is necessary to prepare water-suspendable formulations of these active compounds. For this purpose, the active compounds are ground and mixed with emulsifiers, dispersants and optionally other additives. The preparation of such formulations is described for example in DE 28 11 828 and DE 32 40 862.

TiO_2, Al_2O_3 and SiO_2 are known to be used as formulation auxiliaries in the preparation of insecticidal formulations. US 51 10 594, for example, describes the use of Al_2O_3 for preparing insecticide-comprising impregnated paper coatings. TiO_2-comprising insecticidal coatings are described in the Application ES-A 20 22 016.

Al_2O_3-comprising formulations of solids are described in EP-A 391 851.

Al_2O_3-comprising insecticidal suspensions are described in JP 01268604 and JP 01258603.

The oxides employed in these formulations improve essentially the physical properties, such as film forming or suspension stability, of the formulation.

Chlorpyrifos-impregnated Al_2O_3/SiO_2 carriers employed for preparing powder formulations are described in JP 01279802. This measure is said to achieve better application through formation of a dust.

The present invention relates to aqueous suspensions of insecticidal active compounds, characterized in that they comprise

a) 0.1 to 12.5 % of an inorganic carrier having a particle size of 1 to 30 µm and bearing a coating of active compound,

b) 2.5 to 10 % of formulation auxiliaries,

c) 62.5 to 97.4 % of water

d) 0 to 15 % of glycerol

(the percentages are % by weight).

The formulations according to the invention are outstandingly suitable for preparing spray liquids for professional use in pest control in the household, in industry, in buildings for livestock, etc. They have excellent storage stability and very good dispersability in water. In addition, they can be produced at an economical price. The solvents selected do not cause any problems for the user.

Preferred active compounds are insecticides used in the hygiene sector and in professional pest control, such as carbamates, pyrethroids, phosphoric esters, and mixtures of these active compounds with synergists.

Suitable carbamates are substituted phenyl and naphthyl carbamates.

Preference is given to:

- 2-isobutylphenyl methylcarbamate,
- 4-dimethylamino-3-methyl-phenyl methylcarbamate,
- 2-isopropoxy-phenyl methylcarbamate,
- 1-naphthyl methylcarbamate,

- m-tolyl methylcarbamate,
- 3,4-xylyl methylcarbamate,
- 3,5-xylyl methylcarbamate,
- 2-[1,3-dioxolan-2-yl]-phenyl methylcarbamate.

Preferred pyrethroids are the compounds with the common names permethrin, cypermethrin, deltamethrin, cyfluthrin and β-cyfluthrin.

Preferred phosphoric esters are the compounds with the common names fenitrothion and trichlorfon.

A preferred synergist for these compounds is piperonyl butoxide.

Particularly preferred active compounds are pyrethroids. A very particularly preferred pyrethroid is β-cyfluthrin.

Inorganic carriers are TiO_2, Al_2O_3, MgO and SiO_2 or their mixtures with one another.

A particularly preferred carrier is Al_2O_3.

The active compounds applied to an inorganic carrier are present at 0.1 to 12.5 %, preferably at 0.1 to 7.5 %, particularly preferably at 0.1 to 5 %. The formulation may additionally comprise: free solid active compound at a concentration of 0.1 to 12.5 %, preferably 0.1 to 7.5 %, particularly preferably 0.1 to 5 %. Free active compound may be present depending on the conditions of manufacture, for example as a result of abrasion. The amount of active compound applied to carriers and of free active compound may vary significantly with respect to each other.

The mean particle size of the carrier to which active compound has been applied, for example of Al_2O_3 or TiO_2, is from 1.0 to 30.0 µm, preferably 5.0 to 25.0 µm, particularly preferably 6.0 to 15.0 µm.

The carrier/active compound system may be of symmetrical spherical or asymmetrical shape. Its particle size is determined by known analytical methods, such as screen analysis.

The coating of the carriers with active compound can be achieved by customary coating processes, such as dipping or spraying and subsequent evaporation of the solvent. The active-compound-coated carrier can then optionally be mixed with additional finely ground active compound and homogenized.

Another option is the in situ preparation of a mixture comprising active-compound-coated carrier and free, finely pulverulent active compound. The preparation of such systems may be controlled in a known manner by varying the concentration of the active compound solution, or the evaporation rate of the solvent, etc.

Additionally, the formulations according to the invention may comprise customary auxiliaries such as emulsifiers, stabilizers, preservatives, antioxidants or odorants.

Suitable emulsifiers are: non-ionic surfactants, for example polyoxyethylated castor oil, polyoxyethylated sorbitan monooleate, sorbitan monostearate, glycerol monostearate, polyoxyethylene stearate, alkylphenyl polyglycol ether, for example according to US Patent Specification 39 48 636 or British Patent Specification 148 010; anionic surfactants, such as sodium lauryl sulfate, fatty alcohol ether sulfates, the monoethanolamine salts of mono/dialkyl polyglycol ether orthophosphoric acid esters and the alkali metal salts of sulfosuccinic acid, for example according to DE 32 40 862; cationic surfactants such as cetyltrimethylammonium chloride, and ampholytic surfactants, such as disodium N-lauryl-β-imino-dipropionate or lecithin.

Suitable stabilizers and antioxidants are sulfites or metabisulfites, such as potassium metabisulfite, organic acids, such as citric acid and ascorbic acid, inorganic acids, such as hydrochloric acid or sulfuric acid, and phenols, such as butylhydroxytoluene, butylhydroxyanisole and tocopherol.

Suitable preservatives are formaldehydes or formaldehyde-releasing agents and derivatives of benzoic acid, such as, for example, p-hydroxybenzoic acid.

Other suitable auxiliaries are: defoamers based on polysiloxane and thickeners based on polysaccharide.

The auxiliaries mentioned may be present in the formulations according to the invention in concentrations by weight of 2.5 to 10 %.

The amount of glycerol is from 0 to 15 %, particularly preferably 7.5 to 12.5 %. The compositions according to the invention are applied simply by diluting the suspension concentrates with the desired amount of water, brief stirring and application to walls etc.

The novel suspension concentrates exhibit outstanding sediment stability.

The invention is illustrated by the examples below.

Example 1

11.8 g	of β-cyfluthrin-coated Al_2O_3 (1) and free active compound
3.0 g	of emulsifier 373 tri(methylstyryl)phenol ethoxylate (29 EO)
11.6 g	of glycerol
0.36 g	of gum xanthan (a high-molecular-weight polysaccharide)
0.025 g	of 96 % strength sulfuric acid, technical
0.1 g	of acrylmethanol mono-hemiformal
73.1 g	of deionized water

(1) Preparation

125.0 g of β-cyfluthrin are dissolved in 2,000 ml of acetone and mixed with Al_2O_3 of a particle size of 4.8 to 22.5 µm, and the acetone is distilled off at 54°C under N_2. β-Cyfluthrin-coated Al_2O_3 carriers are obtained. The amount of free, uncoated active compound is about 20 %. The mean particle size of the free, uncoated active compound is about 11 µm.

Example 2

11.8 g	of β-cyfluthrin-coated Al_2O_3 (2) and free active compound
3.0 g	of baykanol SL (a condensate of a 1- to 2-times sulfonated diaryl ether isomer mixture, Bayer AG)
1.0 g	of baysilon-E (a silicone-containing defoamer, Bayer AG)
3.5 g	of neutral emulsifier based on ethylene oxide and propylene oxide (MW ~ 6,000 g/mol)
0.5 g	of gum xanthan (a high-molecular-weight polysaccharide)
0.025 g	of 96 % strength sulfuric acid, technical
80.175 g	of deionized water

(2) Preparation

125.0 g of β-cyfluthrin are dissolved in 1,750 ml of acetone and mixed with Al_2O_3 of a particle size of 4 to 28 µm, and the acetone is distilled off at 54°C under N_2.

β-Cyfluthrin-coated Al_2O_3 carriers are obtained. The amount of free, uncoated active compound is about 30 %.

The particle size of the free, uncoated active compound is about 6 µm.

Comparative example

11.8 g	of β-cyfluthrin having a mean particle size of ~ 4 µm
3.0 g	of emulsifier 373
11.6 g	of glycerol
0.36 g	of gum xanthan
0.025 g	of 96 % strength sulfuric acid, technical
0.1 g	of acrylmethanol mono-hemiformal
73.1 g	of deionized water

Example A

Test for residual action

Test method

Formulation: SC = suspension concentrate.

Surfaces: PVC (Tarket spezial, light green, Article No. 657.427.52), painted plywood (paint: Herbol Malerqualität white, 301 RAL 9010), unglazed tiles (Villeroy und Boch, Art. 2103, Col. 435, Nuance 558), (Size: 15 x 15 cm = 225 cm^2)

Test: Blattella germanica L 5, Blatta orientalis L 5

Treatment of the surfaces:

Spraying of the surfaces is carried out in a fume cupboard allowing regulation of the air flow in such a way that the spray is not affected. The formulations are dissolved in tap water. Spraying is carried out using a glass nozzle and an air pressure of 0.1 bar from a distance of 13 cm. The application rate is 2.5 cm^3/surface, which, minus the overspray, corresponds to a spray quantity of 100 cm^3/m^2.

Animal material and evaluation:

In each case, 5 test animals are kept on the surfaces within talcumed glass rings (diameter 9.4 cm, height 5.5 cm). One day after treatment and after 1, 2, 3, 4, 6 and 8 weeks and further at four-week intervals, the animals are placed on the surfaces and remain exposed there in each case for 24 hours.

Evaluation was carried out by % knock down after 15, 30 and 60 minutes, and then after 2, 3, 4, 5, 6 and 8 hours. After 24 hours, the

destruction in percent is determined and the animals are taken off the surfaces.

Residual action of β-cyfluthrin of various formulations on various surfaces.

			100 % mortality within 24 hours until weeks		
Test animals	Formulation	Application rate mg a.i./m^2	PVC	painted wood	unglazed tiles
Blattella germanica 5th larvae stage	Example 1	5.0	6	16	12
		7.5	8	20	12
		10.0	12	>28	24
	Comparative example	10.0	4	20	12
Blatta orientalis 5th larvae stage	Example 1	5.0	6	12	>28
		7.5	12	24	>28
		10.0	20	24	>28
	Comparative example	10.0	6	12	>28

Residual action of β-cyfluthrin of various formulations on various surfaces.

			100 % mortality within 24 hours until weeks		
Test animals	Formulation	Application rate mg a.i./m^2	PVC	painted wood	unglazed tiles
Blattella germanica 5th larvae stage	Example 2	5.0	6	16	12
		7.5	8	20	12
		10.0	12	>28	24
	Comparative example	10.0	4	20	12
Blatta orientalis 5th larvae stage	Example 2	5.0	6	12	>28
		7.5	12	24	>28
		10.0	20	24	>28
	Comparative example	10.0	6	12	>28

Patent Claims

1. Aqueous suspensions of insecticidally active compounds, characterized in that they comprise

a) 0.1 to 12.5 % of an inorganic carrier having a particle size of 1 to 30 µm and bearing a coating of active compound,

b) 2.5 to 10 % of formulation auxiliaries,

c) 62.5 to 97.4 % of water

d) 0 to 15 % of glycerol

(the percentages are % by weight).

Novel insectidical suspension concentrates

Abstract

The present invention relates to aqueous suspensions of insecticidally active compounds, characterized in that they comprise

a) 0.1 to 12.5 % of an inorganic carrier having a particle size of 1 to 30 µm and bearing a coating of active copmound,

b) 2.5 to 10 % of formulation auxiliaries,

c) 62.5 to 97.4 % of water

d) 0 to 15 % of glycerol.

COMBINED DECLARATION AND POWER OF ATTORNEY	ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought
on the invention entitled

"NEW INSECTICIDE SUSPENSION CONCENTRATES"

the specification of which is attached hereto,

or was filed on **March 27, 1997**

as a PCT Application Serial No. **PCT/EP97/01568**

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims.

I acknowledge the duty to disclose to the Office all Information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

196 13 974.0	**Germany**	**April 09, 1996**
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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